Practical aspects of alkaline sizing: alkyl ketene dimer in mill furnishes

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ABSTRACT *Two production runs using alkyl ketene dimer (AKD) sizes were analyzed, and material balances for AKD and its hydrolysis products were determined. AKD retention ranged from 69% to 95%. Due to hydrolytic side reactions, the usefully reacted AKD only amounted to 20–38% of the total retained AKD in the reel samples, confirming earlier laboratory observations. The distribution of AKD sizes on furnish components is skewed. Fillers and pulp fines accumulate a major portion of AKD, similar to the distribution of rosin sizes. Size deposited onto long fibers is relatively more efficient. Potentially, there are ways to enhance the deposition of AKD on long fibers.*

KEYWORDS
Additives
Alkaline papermaking
Chemical analysis
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Sizing

Internal sizing is a well-established step in the papermaking process for regulating, or reducing, water absorptivity in many paper and paperboard grades. Selecting the proper hydrophobizing agent depends on the grade and on the processing conditions in the wet end of the machine.

In the November 1990 issue (*1*), I reported the kinetics of AKD reactions, comparing the rate of hydrolysis to the rate of curing. Here, we will look at two production runs using AKD sizes, in which performance and efficiency were analyzed under mill or simulated mill conditions.

Background

Sizing methods

Table I compares the most frequently used sizing systems. The most influential parameter is the desired pH of the wet end. Rosin sizing is the main choice for acidic conditions, and reactive sizes are applied for most alkaline papermaking machines. There is an overlap around pH 6–7, where both dispersed rosin acid and reactive sizes can be used. In the earlier paper (*1*), I commented on the advantages and limitations of the various sizing methods, indicating some of the pertinent publications.

The most frequently used reactive sizes are alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). ASA and AKD are interchangeable in some cases, but each type has its own character. The two differ strongly in their rates of interaction with hydroxy groups. ASA reacts relatively easily with either cellulosic hydroxy groups or water. Consequently, the practical shelf life of an ASA emulsion is short (<2 h).

The rather rapid cellulose esterification reaction allows on-machine curing, which is important for regulating color pickup on the size press. In a competitive reaction, ASA is hydrolyzed with water. The diacid salts formed readily deposit on wet press rolls, frequently causing press picking problems. Also, the ASA-cellulose ester bond is easily hydrolyzed by hydroxy acids such as lactic acid or citric acid, rendering ASA ill-suited for some sizing applications.

AKD emulsions are more stable. The shelf life of a commercial, acid-stabilized AKD emulsion is measured in weeks if not in months. Neither the diketene nor the "allegedly" formed cellulose-ester bonds hydrolyze easily. On the other hand, the curing rate of AKD is rather slow, and its on-machine sizing performance is problematic.

Hydrolysis of AKD

The hydrolysis product of the AKD-water interaction is an inert waxy ketone (**Fig. 1**). The rate of hydrolysis is not negligible, and the dialkyl ketone product exhibits some undesirable properties, including:

- Loss of sizing efficiency
- Increased sizing cost
- Nonreactive waxy ketone by-product
- Increased slipperiness.

As mentioned, the kinetics of AKD reactions were reported in the earlier report, and the rate of hydrolysis was compared to the rate of curing—i.e., to the sizing interaction with cellulose (*1*). The cure-related kinetic values were determined by Lindstrom *et al.* (*2, 3*).

The two commercial size preparations used in the laboratory experiments, Emulsion AP and Emulsion HC, were identified in the November report as well. Briefly, Emulsion AP is a weakly cationic emulsion containing 9% pre-emulsified AKD and 3.5% of emulsifier and stabilizer (mostly cationic starch). Its pH in emulsion is

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about 3.5. Emulsion HC is strongly cationic. It contains 6% AKD along with 9% polymer solids consisting of emulsifier, stabilizer, and promoter (mostly polyamide epichlorohydrin resin, or PAE).

Table II shows two pertinent kinetic parameters. The half lives of the emulsions rapidly decrease either with increasing pH or increasing temperature. If present, promoters accelerate both hydrolysis and esterification (curing) reactions. In an emulsion stabilized by cationic starch (Emulsion AP) at pH 8 and between 30° and 70°C, the half-life ($t_{1/2}$) of the hydrolysis reaction is only 12–24 times longer than that of the cure, indicating that hydrolysis potential is not negligible. The activation energy (E) of hydrolysis is double that of the cure. The temperature sensitivity of the hydrolysis reaction is also greater than that of the esterification reaction (or the sizing reaction, or the "cure"). Consequently, hydrolysis is a practical possibility during alkaline papermaking even when AKD size is used.

Focus of this research

One only can appreciate the practical importance of AKD hydrolysis by observing the actual course of sizing reactions under mill conditions. Therefore, the in-mill performance and efficiency of two important commercial AKD sizes have been followed analytically in two mills.

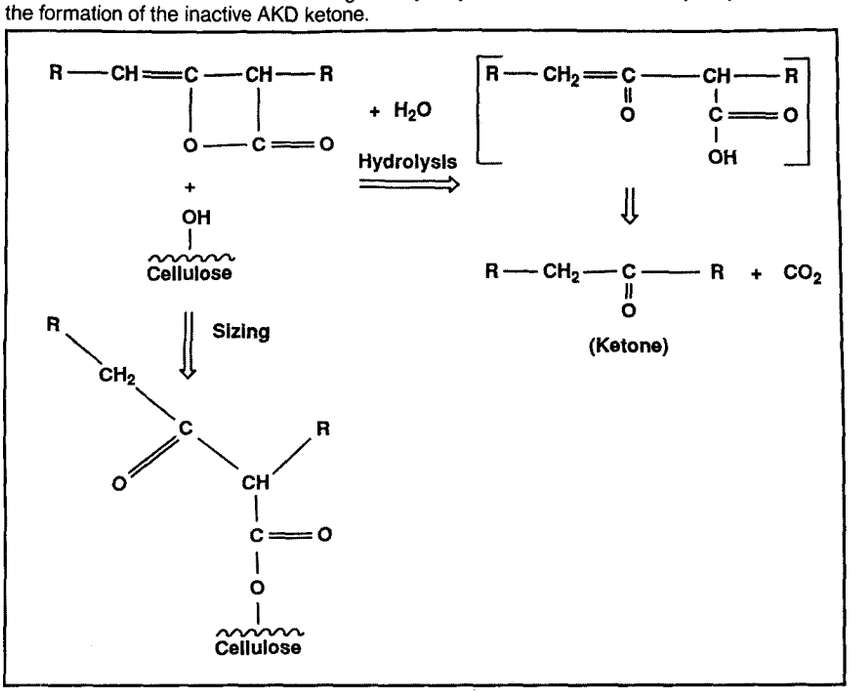
The efficiency of sizing is expressed as the ratio of the usefully reacted AKD to the total AKD-related material retained in the final paper product. The performance of a size is strongly influenced by the adequacy of its retention in the forming web and by the strength of its attachment to the surface of furnish components. In addition, the location of the size on the furnish components may affect its performance. For these reasons, the attachment of AKD size to fiber in a shear field and its distribution between coarse or long fibers and various fillers and fines have been studied also.

Experimental procedures

Size preparations

As mentioned, the two preparations characterized earlier (*1*) were used in the laboratory experiments. Furthermore, Emulsion AP, stabilized with

1. Reaction scheme of cellulose sizing and hydrolysis reactions of AKD. Hydrolysis leads to the formation of the inactive AKD ketone.



I. Comparison of sizing systems

Size	*Optimal pH*	*Advantages*	*Limitations*
Rosin soap-alum	4–5	Reliable, economic, graduated sizing	Higher pH, hard sizing, $CaCO_3$
Rosin acid-alum	5–6	Less alum, higher HST (harder sizing)	Depositions, $CaCO_3$
Rosin acid-PAC	6–7	Pseudo neutral, some $CaCO_3$ tolerance	More expensive Less experience
ASA	6.5–8.5	Fine papers, $CaCO_3$, on-machine sizing	In-mill emulsion, unstable, deposits, no resistance against OH-acids
AKD	7–9	Paper and paperboard, $CaCO_3$, stable emulsion	High filler content, light switch effect, on-machine cure, slippery

II. Kinetic indicators of AKD hydrolysis and cure

Temp., °C	*Hydrolysis*		*AP cure*	*Emulsion AP ratio, hydrolysis/ cure*
	Emulsion HC	*Emulsion AP*		
		Half lives, h		
30	23	140	6	24
50	1.5	27	1.7	16
70	...	3.5	0.3	12
		Activation energy, kJ/mole		
	105	105	55	2

pH = 8.

cationic starch, was also in one of the mills studied (Machine A), while Emulsion HC, stabilized with cationic polymer, was used in the other mill (Machine B).

Methods

The extraction technique and AKD analysis were described earlier (*1*). Other analytical procedures used were conventional. The attachment of the AKD size to coarse, long fiber and the distribution of AKD between the long fiber and the filler and fines were determined at 1000 rpm in the Britt Dynamic Drainage Jar. (Further experimental conditions are indicated in the respective tables.)

Results and discussion

AKD balance

The sampling and analysis of the wet end during regular production or during a production trial can be very informative. **Table III** contains data obtained on Machine A using the Emulsion AP type of size at an average pH of 7.3. The total alkalinity was adjusted by $NaHCO_3$, and a commercial wet-strength additive derived from polyamineamide served as a promoter to curing.

High levels of AKD size were used by the mill to maintain the stringent sizing requirements. The apparent first-pass retention of AKD was around 70%. However, analysis indicates that most of the added AKD hydrolyzed. Only about 20% of the retained AKD material was nonextractible with $CHCl_3$ or other solvents. Both unused original and hydrolyzed AKD are dissolved in the solvent. It is customary to consider the nonextractible part of AKD as the usefully reacted (esterified) AKD. In reality, cellulose fiber cannot react with much more than 0.07% AKD (*1-3*). Analysis indicated that the excess AKD retained was present mostly in the form of the inert ketone. This ketone was shown to contribute little to the sizing performance (*1*). Excessive ketone also can be the source of slipperiness problems.

Table IV shows the AKD balance on Paper Machine B using Emulsion HC. The use of about 2 lb/ton AKD is in the conventional range for filled fine paper stock. Apparent ash retention and AKD retention were quite high. The nonextractible (esterified) AKD portion in the retained AKD was about 38%, a conversion rate on the high side in fine papers (*1*). The remaining 62% was solvent extractible, mainly in the form of the inert ketone (hydrolyzed AKD). Studies of Lindstrom and others (*2, 3*) showed that the usual degree of useful AKD esterification in the laboratory hardly exceeds 50%.

The earlier study (*1*) also indicated that the hydrolyzed portion of AKD is a major contributor to reducing the friction coefficient, though it does not substantially increase the Hercules Size Tester sizing values. An analysis of the tray water solids indicates that the nonretained fines and fillers carry a good portion of the applied AKD. Tray water solids also are enriched with adsorbed alum and cationic starch. This exposure to hot, alkaline tray water during recirculation may explain why the retained AKD material on the solids loses the original reactive diketene groups (as determined by IR analysis of the extract). Wet-end conditions that minimize hydrolysis and increase first-pass retention are factors that can promote efficient utilization of the size on the machine.

Attachment of size

A main condition for good sizing is the efficient attachment of size to the furnish. The attachment should be strong enough to withstand the shear forces in and after the fan pump. High-speed stirring in a Britt Jar proved to be a useful laboratory tool to test the strength of attachment (*4*). The long coarse fibers have been chosen as a model substrate in this study. These fibers have the smallest hydrodynamic specific surface area (about 1.2 m^2/g) in the furnish. It is expected that the attractive forces operative on the other higher-surface-area particles of the furnish are as large or larger.

In this experiment, AKD size emulsion and long, decrilled fibers were stirred at 1000 rpm for 10 min at pH 8 in the Britt Jar. The solids were separated, and the distribution of AKD was determined between the liquid and fibers (*4*).

Table V presents information on the amounts of AKD recovered with the fibers. The dispersed AKD particles, emulsified and surrounded by a highly cationic polyamineamide polymer in Emulsion HC, became strongly attached to the fiber surface. About 76% of the applied AKD remained associated with the fibers even after they were exposed to high shear. Size attachment with the weakly cationic Emulsion AP (emulsified with cationic starch) was only 20%. The application of an additional cationic poly-DADMAC promoter, a strongly cationic homopolymer of diallyl dimethyl ammonium chloride, provided strong AKD attachment.

This experiment suggests that—under proper electrostatic charge conditions—the emulsified AKD can be strongly attached to the furnish, and the attachment can withstand strong shear forces.

Distribution of additives

Most wet-end interactions are surface related. Furnish components do not participate in surface interactions in direct proportion to their weight percentages in the furnish. Rather, component surface area, surface composition, and other factors determine the adsorptivity of an additive on each furnish component (*5, 6*).

In previous work, it was found that rosin size preferentially accumulates on the surfaces of fines and fillers in higher concentrations than expected from surface area ratios alone. It also was found that the location of the rosin size affects its performance. Rosin exhibits the highest sizing efficiency when deposited on the coarse, long fibers, as opposed to being deposited on the surfaces of the fine particulates. The experimentally determined relative adsorptivity values could be used for predicting the distribution of rosin and other additives among furnish components (*5-7*).

Table VI shows the relative adsorptivity of alum and cationic starch on typical fine paper furnish components at pH 5. Adsorptivity of cationic starch roughly follows the ratio of surface areas. The hydrodynamic surface area is important, but it is not the sole parameter that determines the adsorption intensity. Alum is adsorbed to less extent onto fines and clay filler than expected on the basis of surface area ratios alone. This finding suggests that there is an influence from other factors such as surface composition, surface charge, or the penetration of the adsorbate into the bulk of the adsorbent (*5, 6*).

III. AKD analysis for Machine A

Component	Concentration, % on solids		
	Headbox	Tray water	Reel
Starch	1.0	2.8	...
Alum (adsorbed)	0.5	0.6	...
Ash	1.1	1.5	...
Calcium	<0.1	<0.1	...
AKD			
Recovered	0.36		0.25
Reacted	0.03		0.05
Retained, % of applied			69
Reacted AKD, % of retained			20

pH = 7.3, AKD = 0.4% (in Emulsion AP), polyamineamide epichlorohydrin resin = 0.3%.

IV. AKD balance on Machine B

Component	Concentration, % on solids			
	Headbox	Tray water	Couch	Reel
Starch	0.52	1.3	0.7	2.2
Alum (adsorbed)	0.40	1.9	0.3	0.40
Ash	12.3	37.4	9.9	23.5
Calcium	1.5	5.2	1.2	1.0
AKD				
Reacted	0.03	0.10	0.03	0.03
Retained, %	0.08	0.44	0.08	0.08
Reacted AKD, % of retained				38

pH = 7.1, zeta potential = 0, AKD = 0.11% (in Emulsion HC), 0.22 lb/ton PAM retention aid.

AKD itself is electrically neutral. The size is prepared by emulsification of AKD using either cationic starch or a cationic polymer. Electrostatic attraction assures the attachment of the dispersed size particles to the reactive surface sites of the furnish components. There is great uncertainty in extrapolating the adsorption behavior of cationic starch or that of any other polymer emulsifier to the behavior of the emulsified particle. Therefore, the actual distribution of AKD size in model furnishes was determined directly (*4*).

V. Attachment of AKD size to fiber at 1000 rpm

Emulsion type	Zeta potential, mV	Emulsifier	Promoter	AKD recovered from fiber, % of applied
AP	+17	cationic starch	none	20
AP	>+18	cationic starch	0.1% pDADMAC	72
HC	+40	cationic resin	none	76

Stirred 10 min in Britt Jar at pH 7.5, using 0.25% AKD.

Table VII shows the distributions of AKD size in wet pulp (a blend of 85 parts long fiber with 15 parts pulp fines) and in other binary mixtures (85 parts long fiber with 15 parts filler). In the experiments, 0.45% Emulsion HC was stirred at 1000 rpm with the blend of the respective components in a Britt Jar. After 10 min of stirring, the mixture was separated. AKD concentrations were determined on the separated components.

Fillers and fines accumulated AKD size in quantities not unlike the amounts they adsorb with rosin sizes. High-surface-area fine clay and ground $CaCO_3$ (GCC) coating pigments accumulated significantly more AKD than the corresponding filler grades for most papers. It also is expected (though not proven yet experimentally) that the fine precipitated $CaCO_3$ (PCC) filler will show considerable enrichment, in principle similar in extent to that of the other fine-particle pigments. From a practical standpoint, it is important that, in these model furnishes, a relatively small amount of AKD size is deposited onto the fiber surfaces, so that the size efficiency would be at its highest (*4*).

Improving AKD size distribution and efficiency

One can speculate on potential measures to direct more size to the surface of fibers—for instance, using a pretreatment to reduce the surface area or the adsorbing capacity of the applied fillers. Selecting a proper drying regime also may help. It is possible that part of the unreacted AKD redistributes in the furnish during heat drying, smoothing the skewed AKD distribution before the curing interactions have ended.

The papermaker, in search of optimal conditions, frequently faces a decision as to where and in what sequence to introduce the chemical additives in the furnish. Several factors are to be considered that can affect the nature, kinetics, and dynamics of the interactions at the various application locations. The relative contributions of colloidal and hydrodynamic forces change with location in the stock preparation system:

- The furnish consistency changes from thick stock (>3%) to thin stock (<1%).
- Shear exposure increases in and after the fan pump and screens.
- Interaction and contact times decrease at locations closer to the headbox. Temperature also may increase.

VI. Relative adsorptivity of alum and cationic starch

	Fiber	*Pulp fines*	*Filler clay*	*No. 2 clay*
Relative hydrodynamic surface area	1	6	3	10
Alum, relative adsorption intensity	1	3	2	3
Cationic starch, relative adsorption intensity	1	5	3	4

Weight/weight basis.

VII. Distribution of AKD between fibers and either fillers or fines

	Distribution between fibers and:				
	Fines	*Filler clay*	*Coating clay*	*Filler GCC*	*Coating GCC*
		Ratio of size concentrations			
As is*	12:1	9:1	60:1	9:1	40:1
Ash-free basis	21:1	16:1	100:1	11:1	70:1
		Percentage of applied AKD, % on:			
Fiber	18	25	1	33	1
Fillers or fines	77	69	87	52	86
In solution	11	1	2	1	2
		Ratio of amount of size			
	4:1	3:1	87:1	2:1	86:1

*Since the fibers could not be separated completely from filler, the ratios are expressed either "as is" or on an ash-free basis.

CORRECTION

In an earlier paper by Marton (November 1990), some errors occurred in the tables on pages 140 and 141 in regard to the meaning of the letter n. In the title of Table I, the equation $K=10^3 n \cdot k_h$ should have been $k=10^3 k_h$. Again, in Table III, under "Cure" and under "Hydrolysis," the expression 10^3 n k should be 10^3 k.

In other words, the letter n should not have appeared in these expressions. Elsewhere in the article, n is for the number of samples, as r is the correlation coefficient. We apologize for the confusion these errors may have caused.

Incidentally, the activation energy E is calculated from the Arrehenius equation, where the slope of the plot of log k vs. $1/T$ is equal to $E/2.303R$.

Prior to the fan pump, in the thick stock, colloidal forces dominate, and the conditions allow the system to approach an equilibrium state. After the fan pump, hydrodynamic forces dominate; the contact times become shorter, and kinetic effects become increasingly important in adsorption and interactions.

Adsorption of the size directly onto fiber can be enhanced if the size is added to the thick stock before the filler is added.

Another potential tool, though the results are speculative, is high-shear mixing of size and furnish in a medium-consistency (>3%), high-shear pump (*8*) placed in the thick stock line. This concept is based on a hypothesis related to the effect of high shear on enhanced polymer deposition on long fiber in the low-consistency line or in the headbox (*9*).

While some of these ideas are still unproven, we can expect that better understanding of the fundamentals of wet-end chemistry can help the papermaker in improving the performance of sizes and other additives in the papermaking system.□

Literature cited

1. Marton, J., Tappi J. 73(11): 139(1990).
2. Lindstrom, T. and O'Brian, H., Nordic Pulp & Paper Res. J. 1(1): 34(1986).
3. Lindstrom, T. and Soderberg, G., Nordic Pulp & Paper Res. J. 1(2): 39(1986).
4. Marton, J., Sizing mechanisms and effect of fillers, *in* Transactions 8th Fundamental Research Symp., Mech. Eng. Publ. Ltd., London, 1985, p. 785.
5. Marton, J., Tappi 63(2): 121(1980).
6. Marton, J., Tappi 63(4): 87(1980).
7. Marton, J., Nordic Pulp Paper Res. J. 4(2): 77(1989).
8. Marton, J., Some interactions of retention aids with fillers and fines in fine paper furnishes *in* Preprints of EUCEPA International Symposium, EUCEPA, Helsinki, 1990, p. 105.
9. van de Ven, T. G. M., Physicochemical and hydrodynamic aspects of fines and filler retention *in* Trans. 9th Fundamental Res. Symp., Mech. Eng. Publ. Ltd., London, 1989, p. 471.

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